

# Contact glow discharge electrolysis: a study on its origin in the light of the theory of hydrodynamic instabilities in local solvent vaporisation by Joule heating during electrolysis

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## Abstract

Normal electrolysis at high voltages switches over spontaneously to contact glow discharge electrolysis. The transition is profoundly facilitated by raising the temperature and/or lowering the surface tension of the electrolyte. Results of a systematic study on the influence of these two factors on the breakdown voltage for normal electrolysis have been critically analysed. It has been concluded that solvent vaporisation near an electrode by Joule heating during electrolysis and the onset of hydrodynamic instabilities in local solvent vaporisation are the prime causes for the breakdown of normal electrolysis. © 1997 Elsevier Science S.A.

*Keywords:* Contact glow discharge electrolysis; Hydrodynamic instabilities

## 1. Introduction

Contact glow discharge electrolysis (CGDE) is an unconventional electrolysis where electrochemical processes occur in glow discharges at a plasma/electrolyte interface. The phenomenon develops spontaneously at an electrode during conventional electrolysis whenever the applied voltage is sufficiently high irrespective of the electrolyte being aqueous, non-aqueous or molten. The onset of CGDE is marked by a steep drop in the current with the simultaneous appearance of a luminous sheath of gas at either the cathode or the anode. The electrode where the current density is larger, electrolyte resistivity is higher or electrolyte surface tension is lower tends to be the centre of CGDE [1–4]. A remarkable feature of CGDE is that its chemical yield at the glow discharge electrode is several times the Faraday law value and the products are novel for conventional electrolysis such as H<sub>2</sub> at the anode and O<sub>2</sub> at the cathode, etc. [1,2,5–7]. A good number of studies have been reported on the origin and chemical effects of the phenomenon [1–17] as well as spectroscopy of its light emission [18,19]. However, there are several important aspects which need systematic investigation.

It has been inferred from some of the evidence that the

gaseous sheathing over an electrode is caused by a film of solvent vaporised locally due to Joule heating [1,2]. Although the view has been favoured by subsequent studies [3–7,9], a few of these are inclined to consider the volumetric rate of electrolytic gas evolution as a significant factor and even the determining factor for the transition of normal electrolysis to CGDE [9–12]. The aspect thus needs further probing. The mechanism of the growth of a stable gaseous sheath which is steadily anchored to the contour line of the electrode well underneath the electrolyte solution during normal electrolysis is of intrinsic interest and calls for a systematic investigation. Two variables which have been found to influence profoundly the breakdown of normal electrolysis in the transition to CGDE are electrolyte temperature and surface tension. Herein, the results of a study on the influence of these two factors on the transition from normal electrolysis to CGDE are discussed in the light of the theory of hydrodynamic instabilities in solvent vaporisation near an electrode due to Joule heating during electrolysis.

## 2. Experimental

The work was carried out by studying current–time ( $I-t$ ) as well as current–voltage ( $I-V$ ) characteristics of electrolysis under the following set of standard conditions:

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cell, symmetrical Corning H-type (height 11 cm; diameter, 30 mm) having a 7.5 cm long bridge (diameter, 15 mm) fitted with a G-5 sintered glass disc separator at a height of 1.5 cm from the base of the cell; anode, platinum wire of length 5 mm and diameter 0.35 mm; cathode, usually a platinum foil (1 cm × 1 cm) of 0.20 mm thickness, although a 5 mm long platinum wire of 0.35 mm diameter (i.e. identical with the anode) was used in the study on  $I-t$  characteristics; the electrodes were dipped to a depth of 3 cm; electrolytes, aqueous 0.05 M  $K_2SO_4$  (the reference inert-type electrolyte) with or without a surfactant additive (sodium dodecyl sulphate (SDS), *N*-cetyl *N,N,N*-trimethyl ammonium bromide (CTAB) or Aerosol OT at varying concentrations). Surface tension was measured by a precalibrated stalagmometer; pressure, atmospheric; ambient temperature,  $(32 \text{ to } 82) \pm 2^\circ\text{C}$ . Current was supplied from an Aplab-7322 medium voltage d.c. power supply which provided a maximum current of 1.5 A at voltages up to 600 V. The current passing through the cell and voltage across the circuit were measured using a Philips PM2518X digital multimeter.

### 3. Results and discussion

#### 3.1. Current–time characteristics at different temperature

The current–time ( $I-t$ ) characteristic of electrolysis of 0.05 M  $K_2SO_4$  between identical platinum wire electrodes at an applied voltage of 100 V at  $45 \pm 2^\circ\text{C}$  (Fig. 1) consists of an almost linear part PQ representing normal electrolysis followed by a transition period QR. At R, where the current drops by a large amount (325 mA), a gaseous mantle of pulsating thickness develops at the anode and the situation stabilises. The fluctuation in current diminishes with further progress in time up to the point S beyond which a stable gaseous film forms around the anode. Fig. 1 further shows that when the ambient temperature is raised to  $75 \pm 2^\circ\text{C}$ , the formation of the gaseous sheath (corresponding to the point R) occurs much earlier. This can be explained as a higher electrolyte temperature would require less Joule heating for local vaporisation and thus facilitate the vapour sheathing on the electrode which results in the breakdown of normal electrolysis. It is worth noting that the maximum current passing through the cell just before gas sheathing the electrode (the point Q, Fig. 1) is considerably reduced (580 mA to 420 mA) on raising the temperature from  $45^\circ\text{C}$  to  $75^\circ\text{C}$ .

If the rate of electrolytic gas evolution can be considered as the prime cause for the breakdown of normal electrolysis, raising the temperature, which causes lowering of the current maximum (corresponding to the point Q) and consequently a significant lowering in the volumetric rate of electrode gas evolution, would not have facilitated the electrode gas sheathing and the breakdown of normal electrolysis. Moreover, when the ambient temperature is

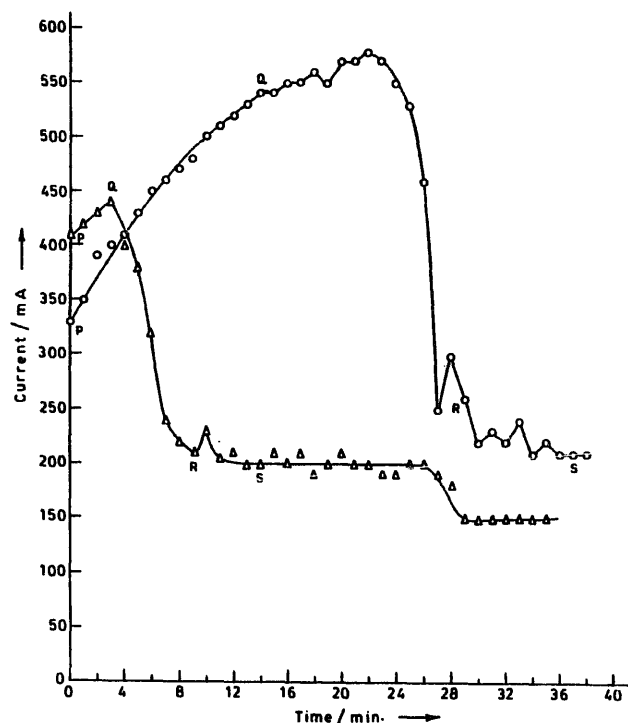


Fig. 1. Current–time ( $I-t$ ) characteristics of electrolysis of 0.05 M  $K_2SO_4$  solution at 100 V for transition to anodic CGDE between Pt-wire electrodes (length 5 mm and diameter 0.35 mm) at two different temperature: (—○—)  $45 \pm 2^\circ\text{C}$  and (—△—)  $75 \pm 2^\circ\text{C}$ .

lowered below  $20^\circ\text{C}$ , Joule heating becomes insufficient to cause solvent vaporisation and no breakdown of normal electrolysis could be observed even at 600 V, although the current passing (1040 mA) and the rate of gas evolution is several times that which can cause the breakdown at a higher temperature. The same conclusion is also arrived at from the results of the effect of temperature on current–voltage ( $I-V$ ) characteristics of electrolysis, the breakdown voltage for normal electrolysis  $V_B$  and the current passing at  $V_B$  falling from (320 V, 670 mA) to (160 V, 410 mA) on raising the temperature from  $35^\circ\text{C}$  to  $75^\circ\text{C}$ . The results of the study thus confirm the soundness of the earlier view point [1,2] that the primary cause for the breakdown of normal electrolysis is vaporisation of the solvent due to Joule heating in the vicinity of an electrode.

#### 3.2. Effect of anolyte surface tension

The present body of evidence is strongly in favour of the view that solvent vaporisation and not electrolytic gas evolution at the electrode is the prime factor for the breakdown of normal electrolysis there. The question arises: how do vapour bubbles formed at an electrode coalesce and form a stable sheath of vapour around the electrode well underneath the electrolyte solution? It is thus of interest to study the influence of the electrolyte surface tension on gaseous sheathing on the electrode resulting in the breakdown of normal electrolysis. It has

Table 1

Verification of the correlation  $j_c \gamma^{1/2} = \text{constant}$  (anolyte, 0.05 M  $\text{K}_2\text{SO}_4$  containing varying concentrations of SDS or CTAB; catholyte, 0.05 M  $\text{K}_2\text{SO}_4$ ; anode, Pt wire of length 5 mm and diameter 0.35 mm; cathode,  $1 \text{ cm}^2$  Pt foil of thickness 0.2 mm; ambient temperature,  $75 \pm 2^\circ\text{C}$ )

Surfactant	$\gamma_{\text{Anolyte}} / \text{mNm}^{-1}$	$V_B^a / \text{V}$	$I_c^b / \text{mA}$ ( $\pm 3\%$ )	$j_c^c / \text{mA cm}^{-2}$ ( $\pm 3\%$ )	$j_c \gamma^{-1/2} / \text{mA cm}^{-2}$ ( $\text{mNm}^{-1}$ ) <sup>-1/2</sup> ( $\pm 3\%$ )
None	63.22	160	490	8910	1120.6
0.25 mM SDS	37.28	160	460	8360	1368.8
0.50 mM SDS	30.32	130	390	7090	1286.9
0.50 mM CTAB	35.16	140	390	7090	1195.8
1.0 mM CTAB	29.99	140	340	6180	1128.1
5.0 mM CTAB	23.16	130	330	6000	1247.4
40 mM CTAB	19.29	120	330	6000	1366.4
60 mM CTAB	19.21	110	340	6180	1411.4
70 mM CTAB	19.19	100	285	5180	1183.1
80 mM CTAB	18.98	100	310	5640	1292.8

<sup>a</sup> Breakdown voltage for normal electrolysis.

<sup>b</sup> Critical current, the maximum current corresponding to  $V_B$  on  $I-V$  curves.

<sup>c</sup> Critical current density.

been shown that surface tension has a profound effect on the transition of normal electrolysis to CGDE [4]. Addition of a surfactant to the anolyte decreases the breakdown voltage  $V_B$  (for normal electrolysis) at the anode as well as the current at  $V_B$  (to be called the critical current  $I_c$ ) to a significant extent whether the surfactant added to the anolyte is cationic (CTAB) or anionic (SDS) (Table 1). Thus, lowering of surface tension promotes considerably the growth of vapour film at the electrode. This aspect is discussed further in Section 3.3.

### 3.3. Applicability of the theory of hydrodynamic instabilities in solvent vaporisation near an electrode by Joule heating during electrolysis

The observed effect of electrolyte surface tension on the transition of normal electrolysis to CGDE is highly interesting. It is well known that according to the static theory of contact angle, lowering of anolyte surface tension would enhance the wettability of the anode and hinder the growth of bubbles on it and thus raise the breakdown voltage  $V_B$  for normal electrolysis, whereas the observed effect is just the opposite. A similar effect of surface tension is observed on the growth of a phenomenon known as 'burn-out' or 'boiling crisis' [20]. This develops in the course of boiling a liquid in contact with a heating solid surface when the surface becomes blanketed by a continuous permanent sheath of vapour resulting in a sharp drop in the specific heat flow from the surface to the liquid. This occurs when the rate of vaporisation vis à vis the specific heat flow goes beyond some critical value. The onset of 'boiling crisis' is significantly facilitated by lowering of

surface tension of the liquid. Furthermore, there is a strong analogy in the morphological events of vapour or gas evolution leading to the onset of both CGDE and 'boiling crisis'. The  $I-V$  (current-voltage) characteristics of electrolysis changing over to CGDE and  $\phi-\Delta T$  (specific heat flow,  $\phi$  vs. surface temperature relative to the liquid  $\Delta T$ ) characteristics of boiling changing over to 'boiling crisis' are very similar.

It appears that there is a basic cause common to the two phenomena. The onset of 'boiling crisis' is well explained in terms of the conditions of hydrodynamic instabilities described by Helmholtz and by Taylor [20–24]. So, it is worth examining the applicability of the hydrodynamic approach in solvent vaporisation at an electrode due to Joule heating during electrolysis. Such an approach based on the Helmholtz and Taylor instability conditions in gas evolution at an electrode during molten salt electrolyses has been fairly successful in explaining the growth of anode effect (anodic CGDE) in molten salt electrolyses [25]. A similar line of reasoning was advanced for aqueous salt electrolyses [10,11].

However, as inferred from the present study, solvent vaporisation and not electrode gas evolution is the prime factor for the breakdown of normal electrolysis. It is thus worth attempting the hydrodynamic approach in solvent evaporation at an electrode during electrolysis to understand the mechanism of breakdown of normal electrolysis. According to this approach, when the rate of vapour evolution at an electrode attains the critical value for the onset of instabilities, streams of vapour bubbles in the electrode region would have their vapour/liquid boundary surface broken and also become close enough to coalesce into a continuous gaseous blanket on the electrode. An increase in surface tension would hinder the onset of hydrodynamic instabilities. A proportionality between the critical rate of solvent vaporisation  $R_c$  and the critical electrolytic current density  $j_c$  (which corresponds to the current at breakdown voltage  $V_B$  on the  $I-V$  curve) may be postulated. For the case of wire electrodes of radius  $r$ , having high enough length to radius ratio, two correlations would follow [10,11,20]:

$$j_c r^{1/2} = \text{constant for a given electrolyte surface tension;}$$

$$j_c \gamma^{-1/2} = \text{constant for a given electrode.}$$

from the expression for the critical rate of solvent vaporisation  $R_c$  at wire electrodes of radius  $r$

$$R_c = \left[ \frac{\rho_L \gamma}{\rho_G (\rho_G + \rho_L)} \right]^{1/2} \times \left[ \frac{g}{\gamma (\rho_L - \rho_G)} + \frac{1}{(r + \Delta r)^2} \right]^{1/4}$$

where  $\rho$  is the density,  $g$  is the acceleration due to gravity,  $\Delta r$  is the thickness of the vapour layer,  $L$  (sub-

Table 2

Verification of the correlation  $j_c r^{1/2} = \text{constant}$  (anolyte, 0.05 M  $K_2SO_4$  containing surfactant; catholyte, 0.05 M  $K_2SO_4$ ; anode, 5 mm long Pt wires of different radii; cathode, 1 cm<sup>2</sup> Pt foil of thickness 0.20 mm; ambient temperature,  $32 \pm 2^\circ\text{C}$ )

Sr. No.	Surfactant	Surface tension $\gamma/\text{m N m}^{-1}$	Anode (wire) radius $r/\mu\text{m}$	$V_B^a/\text{V}$	$I_c^b/\text{mA}$ ( $\pm 3\%$ )	$j_c^c/\text{mA cm}^{-2}$ ( $\pm 3\%$ )	$j_c r^{1/2}/\text{mA cm}^{-3/2}$ ( $\pm 3\%$ )
1	None	69.58	175	320	930	12180	1608.0
2	None	69.58	250	400	1180	8920	1408.9
3	0.50 mM SDS	36.68	100	200	225	7160	716.6
4	0.50 mM SDS	36.68	175	290	400	7270	960.0
5	0.50 mM SDS	36.68	250	300	420	5350	845.4
6	70 mM CTAB	25.55	100	150	320	10190	1019.1
7	70 mM CTAB	25.55	175	220	500	9090	1200.0
8	70 mM CTAB	25.55	250	250	650	8280	1308.0
9	10 mM Aerosol OT	18.55	100	150	370	11803	1178.3
10	10 mM Aerosol OT	18.55	175	180	480	8730	1152.0
11	10 mM Aerosol OT	18.55	250	190	490	6240	986.2

<sup>a</sup> Breakdown voltage for normal electrolysis.

<sup>b</sup> Critical current, the maximum current corresponding to  $V_B$  on  $I$ - $V$  curves.

<sup>c</sup> Critical current density.

script) denotes liquid, G (subscript) denotes gas, neglecting  $(g/\gamma)(\rho_L - \rho_G)$  with respect to  $1/(r + \Delta r)^2 \approx 1/r^2$ ,  $\Delta r \approx 0.01$  mm [2] is much less than  $r$  (0.10–0.25 mm) selected in the study.

Obviously, it is of basic interest to examine the applicability of the two correlations for the breakdown of normal electrolysis of an electrolyte containing varying concentrations of different surfactants and for wire anodes of different radii. The results obtained on the correlation between the critical current density  $j_c$  for a 5 mm long platinum wire anode of 0.175 mm radius and surface tension  $\gamma$  of 0.05 M  $K_2SO_4$  anolyte containing varying concentrations of SDS or CTAB (Table 1) are quite encouraging. In spite of significant variations in surface tension of the anolyte medium, values of  $j_c \gamma^{-1/2}$  were found to remain fairly constant within  $\pm 6.8\%$ . Further, the nature of charge on the surfactant ion does not influence the results. Thus, according to the hydrodynamic theory, lowering of surface tension acts in the sense of breaking up the gas/liquid interface in the streams of vapour bubbles over the anode and thus facilitates the coalescence of bubbles leading to vapour sheathing of the entire electrode surface and consequently the breakdown of normal electrolysis at a lower  $j_c$  and hence lower  $V_B$ . The other correlation  $j_c r^{1/2} = \text{constant}$  within  $\pm 6.3\%$  has also been found applicable over a significant range of the values of the radii of the anode wire (0.10 to 0.25 mm) whether the anolyte contains any surfactant or not (Table 2). This explains the observation that the breakdown of normal electrolysis occurs easily at a thinner wire electrode (Table 2). An electrode of lower radius would require a higher  $j_c$  ( $j_c r^{1/2} = \text{constant}$ ) and thus a lower  $I$  ( $I = \text{constant} \times 2lr^{1/2}$ , where  $l$  is the length of the wire) and a lower breakdown voltage  $V_B$ .

Thus the sequences of events leading to fully grown CGDE can be described as normal electrolysis, solvent vaporisation by Joule heating near an electrode, onset of hydrodynamic instabilities leading to complete and steady

vapour sheathing over the electrode and glow discharges across the sheath.

#### 4. Conclusions

All these results indicate that solvent vaporisation close to an electrode due to Joule heating, not electrolytic gas evolution, and the onset of hydrodynamic instabilities in solvent vaporisation at the electrode, are the two prime factors for the transition of normal electrolysis to CGDE. The conditions of higher electrolyte temperature, lower electrolyte surface tension and thinner electrode favour the breakdown of normal electrolysis.

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